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## THERMOCHEMICAL MODIFICATION OF THE SURFACE OF A MOVING GLASS RIBBON

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The results of studies of thermochemical modification of the surface of a glass ribbon in continuous production are presented. It is shown that the deposition of a composite coating, which was developed by the present authors, on the surface of the glass increases its water resistance by an order of magnitude and the mechanical strength about 2-fold. The essence of the proposed development lies in the deposition in several stages of chemical reagents which create on the surface of the glass a transparent film that permits controlling the quality of the float-ribbon.

**Key words:** float-ribbon, thermochemical modification of a glass surface, water-resistance of glass, mechanical strength of glass.

Sheet glass has a substantial place among the various materials now used in technical structures and buildings.

Owing to its unique property — transparency together with strength and hardness, in a number of cases it cannot be replaced by any other material. The percentage of glass can exceed 80% in modern buildings.

In order to guarantee the safety of the glazing of tall buildings and the durability of glass articles in service the mechanical strength of glass, as the main service characteristic of glass, must be increased [1].

It is known that the mechanical strength of float-glass is a statistical quantity and is characterized by a large variance of its values (from 20 to 200 MPa). For this reason, the most likely statistical value of the strength or of the minimum values of the strength should be taken as the guaranteed opera-

ting characteristics. Such indicators can be introduced into the standards for construction glass.

Approximately 40% of construction glass is lost during storage, transportation, and mounting. This is because initially the float-glass is too weak and its strength decreases because of corrosion. Stacked sheets of glass are exposed to the humid atmospheric air and temperature differentials, which can result in the appearance of defects such as surface leaching. For this reason, the water resistance of construction glass is also its service characteristic, and the problem of increasing the water resistance is urgent.

The operating properties of sheet glass (strength and water-resistance) are determined mainly by state of its surface.

It is well known that because of the particulars of its technology the properties of float glass show a substantial variance along the width of and between the surfaces of the ribbon. This is especially true for the mechanical strength of glass (Table 1).

**TABLE 1.** Statistical Average Values of the Mechanical Strength and the Water-Resistance of Float-Glass Surfaces

Glass surface	Glass strength under symmetric bending, MPa			Coefficient of asymmetry of the strength of the surfaces	Water-resistance mg Na <sub>2</sub> O/dm <sup>2</sup>	Coefficient of asymmetry of the water-resistance of the surfaces $K_a$
	minimum	maximum	average			
Top	98	343	224	2.1	0.227	1.6
Bottom	39	257	107		0.139	

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Eliminating the asymmetry of the surface strength of float-glass and equalizing it over the width of the ribbon during extraction will make it possible to obtain glass with highly stable strength and to solve the problem of standardizing the indicators of these properties.

Various scientific organizations in Russia and abroad have now performed a great deal of work on improving the service properties of sheet glass and glass articles. The main direction of these works is thermochemical modification of a glass surface by means of different reagents [2 – 4].

However, thermochemical hardening of a float-ribbon during extraction, which would make it possible to decrease the variance of the strength over the glass ribbon width and eliminate the asymmetry of the surface properties, has still not been accomplished.

This is because all requirements for the modifying reagents were not met for a moving glass ribbon: uniformity of the distribution of the reagents over the surface of the glass, uniformity and transparency of the strengthening coatings, possibility of using cullet in glassmaking, environmental safety of the reagents used, and so on.

We have conducted a search of the scientific-technical information concerning the improvement of the service properties of glass. This revealed about 1500 modifying reagents in different combinations and aggregate states.

A summary table of the advantages and disadvantages of the reagents examined from the standpoint of the suitability for deposition on the surface of a float-ribbon, the state of the modified surface, and the operating properties of the float-glass was constructed. Analysis showed that the gaseous reagents meet practically all requirements for coatings and improve somewhat the strength properties of the glass, but they are not widely used in production because of their toxicity and short diffusion depth of the reagent particles in the glass.

It is known that the rate of the diffusion processes depends on the capacity of a reagent to form ions, the temperature and action time of the reagent, and the concentration of the reagent. Since the time and temperature intervals where the reagents act on the glass ribbon are limited by the possibilities of the technological process, liquid reagents emerge in first place because of their ability to form ions. However, a universal reagent which would make it possible to improve the service characteristics of glass has still not been found.

Thus the work was focused on the development of mixes of compounds and methods for depositing them on a moving glass ribbon.

On the basis of the analysis of the published data three groups of chemical reagents which could be used for thermochemical modification of the surface of a float-ribbon were identified according to the type of action on the glass. These are salts of inorganic acids which give rise to compressive stresses, silicon-organic compounds which can "heal" microcracks, and polymer compounds which lead to surface conservation.

Different forms of the modifying reagents and compositions based on them (about 160 variants) were tested at the

**TABLE 2.** Change of the Operating Properties of Glass Treated with Different Modifying Reagents

Reagent type	Degree of improvement of the service indicators of glass	
	mechanical strength	water-resistance
Polymethylsiloxane (PMS)	2.0	2.0
Composition of cold coating (CCC)	1.7	1.1
Composition for hot hardening (CHH)	1.7	10.3
CHH and CCC	2.0	9.8
Sulfur dioxide	1.2	1.6

laboratory stage of the investigations; the deposition temperatures for the coatings on glass samples were found; and, the operating properties of the glass were measured. The most effective compositions are given in Table 2.

Evidently, the best result is obtained when glass samples are treated with a composition for hot hardening (CHH), which increases its water-resistance by an order of magnitude. Treating glass with sulfur dioxide, which is conventionally used in float-glass production, increases water-resistance only 1.5-fold.

The investigations showed that the CHH thermochemical treatment of glass engenders structural changes in the near-surface layer of the glass ribbon at depths  $\sim 5 \mu\text{m}$ , and the treatment of float-glass with sulfur dioxide does so to depth  $0.5 \mu\text{m}$ .

The results of the investigations were used as a basis to choose two types of modifying compositions and propose a method for hardening a moving ribbon of float-glass. This method included two stages.

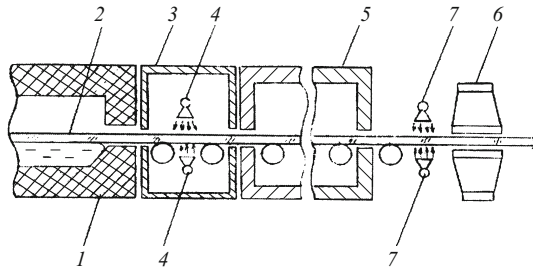
*Stage I* includes modification of the glass surface by the composition for high hardening (CHH) at  $600^\circ\text{C}$ . The solution is deposited by aerosol spraying (using nozzles) on both surfaces of the glass ribbon after it leaves the melt tank. In addition, solutions with different concentration are used for the top and bottom surfaces in order to eliminate the existing asymmetry of the strength properties of the surfaces.

*Stage II* consists of treating the glass surfaces with a solution of the composition for cold coating at  $250^\circ\text{C}$ . The water solution of this reagent is likewise applied with different concentration. The coating formed has a protective function; it prevents the formation of microcracks on the glass surface.

Figure 1 shows a schematic diagram of the method of two-stage hardening of a glass ribbon.

The facility for depositing the hardening reagents consists of a multifunctional moving rack to which nozzles are attached, making it possible to treat the surface of the moving glass ribbon in several stages at temperatures from  $70$  to  $600^\circ\text{C}$  depending on the type of reagent used and the required properties of the glass.

The proposed two-stage treatment gives a transparent film, which does not impede quality monitoring of the float-



**Fig. 1.** Schematic diagram of the method of two-stage hardening of a moving ribbon of float-glass: 1) melt tank; 2) float-glass ribbon; 3) slag chamber; 4, 7) nozzles; 5) closed part of the annealing furnace; 6) open part of the annealing furnace (blower).

ribbon. It should be noted that glass treated with these reagents can be used with recycled cullet, since it contains uniform elements which are part of the composition of the glass mass and the protective-gas atmosphere. In addition, these reagents are environmentally safe, so that the question of salvaging them does not arise. Since the solutions used are water solutions, their concentration in air and standing water is much lower than maximum admissible amount (MAA).

The investigations showed that the two-stage treatment of a glass surface by the compositions developed made it possible to increase its water resistance by an order of magnitude and increase the mechanical strength approximately 2-fold. The minimum values of the strength were increased approximately 4-fold, as a result of which the variance in the values over the width of the ribbon decreased considerably. In addition, the existing asymmetry of the hardness of the glass surfaces was practically eliminated (Tables 3 and 4).

The most suitable zones for depositing the modifying reagents were chosen on the basis of the laboratory and experimental work, and the initial requirements for the commercial prototype equipment were developed.

The fundamental innovation proposed for adoption is deposition of environmentally harmless hardening reagents in several stages. This will make it possible not only to increase the strength indicators considerably but also to equalize them over the surface area. The method described can be easily built into the float-glass production process and substantially decrease the losses of the finished product in storage, transportation, and operation.

**TABLE 3.** Water-Resistance of the Molded Surfaces of Float-Glass

Glass surface	Water resistance, mg Na <sub>2</sub> O/dm <sup>2</sup>			Water-resistance increase coefficient
	initial glass	after the first treatment stage	after the second treatment stage	
Top	0.227	0.023	0.023	9.8
Bottom	0.139	0.013	0.013	10.3

**TABLE 4.** Mechanical Strength of the Bottom Surface of the Float-Glass

Statistical indicator	Glass strength under symmetric bending, MPa			Strength increase coefficient
	initial glass	after first treatment stage	after two treatment stages	
Minimum value	48.4	77.5	232.4	4.8
Average values	110.2	143.3	270.3	2.5
Maximum values	257.4	298.6	388.2	1.5

The work on adopting thermochemical modification of a moving glass ribbon under the conditions of continuous commercial production will make it possible to develop the required prerequisites for implementing new technologies for obtaining float-glass with prescribed properties.

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